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Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis

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Abstract

The objective of this study was to evaluate the impact of pH on boron, fluoride, and nitrate retention by comparing modelled speciation predictions with retention using six different nanofiltration (NF) and reverse osmosis (RO) membranes (BW30, ESPA4, NF90, TFC-S, UTC-60, and UTC-80A). Retention was explained with regard to speciation, membrane properties, and ion properties such as charge, hydrated size, and Gibbs energy of hydration. Flux was independent of pH, indicating that pH did not alter pore size and hence permeability for all membranes except UTC-60. Membrane charge (zeta potential) was strongly dependent on pH, as expected. Boron and fluoride retention depended on membrane type, pH, which correlated closely to contaminant speciation, and was due both to size and charge exclusion. While retention at low and neutral pH was a challenge for boron, high boron retention was achieved (>70% above pH 11). Fluoride retention was generally > 70% above pH 7. Nitrate retention depended on membrane, and was mostly pH independent (as was the speciation). The presence of a background electrolyte matrix (20 mM NaCl and 1 mM NaHCO₃) reduced nitrate and boron retention (at high pH) due to charge shielding, and enhanced the retention of fluoride in single feed solutions, suggesting preferential transport of Cl⁻ compared to F⁻ with Na⁺.

Keywords: Groundwater, nanofiltration, nitrate, fluoride, boron, stirred cell.

1 Introduction

Available water quantity and quality is an issue of survival in many parts of the world. Groundwater is often considered a viable drinking water resource but may contain chemical contaminants such as boron (B), fluoride (F), and nitrate (NO₃⁻), which have respective World Health Organization guidelines of 0.5 mg/L (provisional), 1.5 mg/L, and 50 mg/L (short term exposure), respectively [1]. Concentrations of boron, fluoride, and nitrate in water supplies are reduced by varying degrees by the use of nanofiltration (NF) and reverse osmosis (RO) [2-5].

Boron exposure is associated with short-term irritant and organ effects, however chronic toxicity in humans has not been clearly defined. Conventional water treatment processes such as coagulation, sedimentation, and filtration are ineffective at boron removal [6], but NF/RO are commonly used [2, 7]. Fluoride exposure via drinking water of concentrations above 1.5 mg/L can lead to dental fluorosis, and greater than 10 mg/L can lead to skeletal fluorosis [8]. Fluoride removal techniques include membrane filtration, sorption, co-precipitation, and contact precipitation [8]. Nitrate in drinking water is of concern mainly due to its reduction to nitrite, which is toxic and leads to methaemoglobinaemia (baby blue syndrome) causing reduced oxygen transport to bodily tissues and particularly dangerous for infants [9]. Nitrate treatment techniques involve membrane processes, oxidation, ion exchange, biological denitrification, and source management [9]. NF/RO can be effective treatment processes for each of these contaminants and thus is the focus of this study.

NF/RO retention depends on solute and membrane characteristics as well as operating conditions (in particular pH and pressure) [10, 11], and is impacted by a number of mechanisms including Donnan equilibrium (charge repulsion), steric hindrance, and differences in diffusivity and solubility of solutes [12, 13]. Solution pH, which is the focus of this study, is very important because it affects not only the different forms (species) in which a solute is present in a solution (changing properties such as size, charge and hydration), but membrane characteristics (such as charge and pore size) as well [14]. Thus, pH can impacts both water flux and solute retention mechanisms (namely charge and size interactions), making pH an important parameter for ion retention in NF/RO.

Solute speciation depends on the specific conditions of the feed solution, including pH, ionic strength, total elemental concentrations, temperature, and pressure [15]. Different species of the same solute have different characteristics such as size and charge, which affect retention mechanisms. For example, if an uncharged solute is deprotonated at its pK_a, charge exclusion may become significant. A change in species affects hydration state and consequently hydrated radius, thus impacting retention when size exclusion is important [16, 17].

Membrane characteristics such as zeta potential [18] and hence retention properties are affected by pH. Solution chemistry, in particular the presence of salts containing divalent ions, impacts zeta potential due to the preferential adsorption of divalent cations rather than divalent anions to the membrane surface especially in the higher pH range [18]. Generally, increasing feed water pH results in an increasingly negative surface charge for most polymeric membranes. Subsequently, electrostatic interaction between ionic compounds and the membrane surface vary according to solution pH [14], with minimal retention typically occurring around the isoelectric point of the membrane surface due to the minimized electrostatic effects [19-23]. Additionally, pH impacts the

dissociation of the functional groups on the membrane surface which can impact the “openness” of the pores [14]. A study by Childress and Elimelech [14] observed NaCl retention was directly related to membrane pore charge (rather than the membrane surface), with minimum retention at the isoelectric point of the membrane pores. However, this is not the case for all membranes [14]. The importance of pore charge is particularly important for “loose” membranes, when the hydrated radius of the solute is smaller than the pore radius [14, 24]. These studies show that pH can affect both the charge and pore size of the membrane.

The relationship between pH and retention for boron, fluoride, and nitrate has been explored to some extent [2, 4, 5, 25-29], however the focus and novelty of this study is the specific relationship between solute speciation and retention mechanisms for these contaminants. The objective is to systematically evaluate the impact of pH on boron, fluoride, and nitrate retention by comparing speciation with retention using six different NF/RO membranes.

2 Materials and Methods

2.1 Chemicals

Analytical grade boric acid ($\text{B}(\text{OH})_3$), hydrochloric acid (HCl), nitric acid (HNO_3), sodium chloride (NaCl), sodium fluoride (NaF), sodium nitrate (NaNO_3), sodium hydrogen carbonate (NaHCO_3), and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich. $\text{B}(\text{OH})_3$ (1 mg/L as B), NaF (3 mg/L as F), and NaNO_3 (100 mg/L as NO_3^-) were the target solutes, with concentrations selected to be broadly representative of natural groundwater sources [1, 6, 8, 9, 30]. NaCl (20 mM) and NaHCO_3 (1 mM) were used as background electrolyte and buffer, respectively. HCl (1 M) and NaOH (1 M) were used to adjust pH. All solutions were prepared with purified water (MilliQ).

2.2 Filtration System and Membranes

A magnetically-stirred stainless steel batch cell was used for filtration experiments. The total volume of each stirred cell was 185 mL, and the membrane surface area was 21.2 cm². The operating pressure was provided by instrument air and set at 5 bar. Pressure and weight were recorded on a computer using LabVIEW (National Instruments, USA). Figure 1 shows a schematic of the experimental apparatus.

Figure 1

Prior to each experiment, the new membrane was compacted for one hour with a pressure of 10 bar and pure water flux was subsequently determined at 5 bar for 30 minutes. Retention experiments were conducted at 5 bar and pH 3, 5, 7, 9, 11 and 12.5. For each batch experiment, 5 samples of 25 mL aliquots were collected from the feed (25 mL), concentrate (25 mL), and permeate (3 consecutive samples of 40 mL each for a total filtrate of 120 mL). Retention calculations compensated for the increasing feed concentration and decreasing feed volume as a function of time via mass balance.

The flat-sheet membranes used were BW30, ESPA4, NF90, TFC-S, UTC-60, and UTC-80A. Membrane information is available online from the manufacturers (Filmtec, Hydranautics, Koch,

and Toray). Experiments with BW30, NF90 and TFC-S were conducted both in purified water and background solution in single contaminant feed solutions to assess the impact of the background solution on retention. Experiments with UTC-60, UTC-80A, and ESPA 4 were conducted both in purified water and background solution in mixed contaminant feeds. Experiments with NF90 were conducted both in single and mixed contaminant feed solutions (with background) to assess the impact of mixed feed.

2.3 Analysis

A pH meter (Metrohm 744) was used to measure pH. For single feed experiments, nitrate and fluoride were measured using ion chromatography (IC) (Dionex DX-100, A.I. Scientific) with PeakNet software and an autosampler. The column was Dionex AS9-HC, the detector was a conductivity detector, and the eluent used was Na_2CO_3 (9.0 mM, pH=10). For mixed feed experiments, nitrate was analysed using a QuikChem 8500 FIA Nutrient Analyzer (Lachat Instruments, USA) and fluoride with an ion selective electrode connected to an ion meter (Metrohm 781, UK). Boron analysis was conducted with inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2400 DV). Samples for boron analysis were preserved to pH 2 using HNO_3 (1 M), while samples for fluoride and nitrate analysis were not acidified.

2.4 Zeta Potential and Membrane Characterization

Streaming potential of the membrane surfaces was determined using an electrokinetic analyzer (EKA, Anton Paar KG, Austria) with Ag/AgCl-electrodes (SE 4.2, Senortechnik Meinsberg, Germany). The membrane zeta potential was calculated using the Helmholtz-Smoluchowski and Fairbrother-Mastin equations, as described in [18]. Streaming potential was measured in 20 mM NaCl and 1 mM NaHCO_3 .

NF90 and BW30 were additionally characterized for pore size using a hydrodynamic model [31] to fit experimental retention of neutral organic solutes (dioxane, xylose, dextrose, and methanol) following the methodology described in [32].

2.5 Speciation Modeling

Speciation predictions in both purified water and background solution were modeled using Visual MINTEQ (version 2.53) [33], with a fixed carbonate concentration (at a partial pressure of $3.8 \cdot 10^{-4}$ atm), temperature of 25 °C, and methods as previously described [34].

3 Results and Discussion

3.1 Membrane Zeta Potential

Zeta potential for each membrane changed from positive to negative with increasing pH, with the exception of ESPA4 which was never positively charged (Figure 2). The point of zero charge (isoelectric point) of the membranes used was 3.1, 3.2, 4.1, 4.2 and 4.3 for TFC-S, UTC-60,

ESPA4, BW30 and NF90, respectively. Zeta potential was unavailable for UTC-80A. The isoelectric points, pore sizes, and membrane properties are summarized in Table 1.

Table 1

3.2 Flux as a Function of pH

The permeate flux was independent of pH, with the exception of UTC-60, and is shown in Figure 3 for all experiments conducted. The average flux (Table 1) sequence for purified water experiments was UTC-60 > NF90 > ESPA4 > TFC-S > BW30 > UTC-80A. With the background solution, the flux sequence was the same with the exception of TFC-S being greater than ESPA 4. Flux in background was always lower than the corresponding pure water flux with the same membrane, which is attributed to concentration polarization and osmotic pressure effects. The lowest overall flux occurred with UTC-80A, which is an RO membrane developed for high boron retention.

3.3 Speciation and Retention as a Function of pH

Characteristics of boron, nitrate, and fluoride species are summarized in Table 2, including hydrated radii and Gibbs hydration energies where available to compare hydration strength. Hydrated radii are collected from one data source for consistency where possible [35]. Speciation and retention results for each contaminant are shown in Figure 4, Figure 5, and Figure 6. Speciation predictions in purified water and background solution were the same for each solute, showing the additional ionic strength did not impact speciation as sometimes observed at high salt concentration [36].

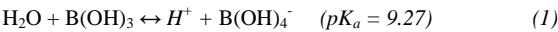
Figure 4

Figure 5

Figure 6

3.3.1 Boron Speciation and Retention

The speciation of boron was dependent on pH (Figure 4A). Dissociation of B(OH)₃ to borate (B(OH)₄⁻) occurred at pK_a = 9.27 [37]. This means that boron predominantly existed in aqueous solution as uncharged B(OH)₃ below pH 9.27 and as B(OH)₄⁻ above pH 9.27 (see equation (1)). No other forms of boron were predicted to be present in solution, and there was no difference in boron speciation in the background solution.



The influence of pH on boron retention was significant (see Figure 5A and B as well as Figure 6 A and B). Retention was very low (< 23%) between pH 3 and 9 for all membranes except UTC-80A. With UTC-80A at low pH retention was approximately 50%, both in purified water and background solution, which is significantly higher than the other membranes. At pH 11 and 12.5, retention

increased significantly for all membranes. Retention with UTC-60 was significantly lower than all other membranes, even at high pH which is likely due to the more open nature of UTC-60 as shown by its high flux. Similar pH effects on boron retention have been previously reported [2, 7, 36, 38-40], however, data on all membranes used in this study have not been reported and the effects of salinity are often neglected. The improved performance of UTC-80A compared to other membranes at lower pH is significant. Although the performance was even better at pH 10-12.5, the practical issues associated with treating waters of high pH are additional chemical cost and risk of scaling and corrosion [38, 41, 42].

The retention pattern correlated closely with the speciation of boron. At acidic and neutral pH, where retention is lowest, boron was present as boric acid B(OH)₃. This neutral species was easily transported through the membrane due both to lack of steric hindrance and lack of charge repulsion. Thus, the higher retention achieved with UTC-80A was likely due to the tight nature of that membrane (which is supported by UTC-80A's low flux).

Above pH 9, retention sharply increased for all membranes (≥ 75% in all cases except for UTC-60 which only reaches 52% in purified water and 30% in background solution). This increase in retention closely corresponded with the speciation change from B(OH)₃ to B(OH)₄⁻ (see Figure 4A), which is anionic as opposed to B(OH)₃ [40]. In consequence, the negatively-charged borate ions experienced electrostatic repulsion by the negatively-charged membranes (Donnan exclusion) at pH 11 and 12.5 [38]. Although specific hydration information of the boron species is not currently available, B(OH)₄⁻ is larger than B(OH)₃ [40] so at pH 11 and 12.5 increased retention can further be explained due to size exclusion.

In addition, differences in retention between B(OH)₃ to B(OH)₄⁻ have been attributed to three-dimensional differences in the molecular structure between the two compounds, which resulted in differences in interactions with membrane active groups [38]. B(OH)₄⁻ has a tetrahedral structure with a sp³ hybrid orbital, in contrast with the trigonal planar structure of B(OH)₃ [43]. The planar structure enhances hydrogen bridges between B(OH)₃ and the membrane functional groups, enabling B(OH)₃ to permeate in a similar manner as carbonic acid or water via convection/diffusion [38]. Functional groups are COOH and amine for BW30 and NF90, and COHN for TFC-S (see Table 1) but details and functional groups of the other membranes are unknown and proprietary.

Boron retention in purified water was higher than in the background solution at pH 11 and 12.5 (up to 22% different for UTC-60, with most notable differences in the mixed feed solutions). This is because at pH 11 and 12.5, B(OH)₄⁻ retention was affected by charge repulsion, and in background solution, the increase in Na⁺ ions (from < 1 mM to 20 mM) shielded charge repulsion. The shielding phenomenon is characteristic of charged membranes and has been commonly used to explain decreased anion retention in the presence of increased ionic strength [4, 27, 44, 45]. In single feed solutions, from pH 3 – 9, there was no difference in neutral B(OH)₃ retention with and without the background solution, which is consistent with the observation that charge becomes important at pH 11 and 12.5. A comparison of single feed and mixed feed with NF90 in background solution (Figure 5 and 6 B) showed slightly lower retention of B(OH)₃ in the mixed feed solution of higher ionic strength (10% in mixed feed; 20% in single feed).

3.3.2 Nitrate Speciation and Retention

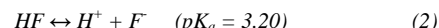
The speciation of nitrate does not depend on pH, with >99.5% present in ionic form (NO₃⁻) (see Figure 4B). No difference in speciation of nitrate occurs in background solution.

Nitrate retention (Figure 5C and D; Figure 6 C and D) varied widely from 20 – 96%. Retention was 60-96% and mostly pH independent for RO membranes BW30 and UTC-80A, showing that size exclusion is important when pore size is smaller than or similar to solute size. For other membranes, retention was mostly pH independent above the isoelectric point of the membranes (it shows the same shape for all membranes). Because NO_3^- was of uniform charge and the charge of all membranes increased with pH, a continuous increase in retention with pH would be expected if charge exclusion was dominant. Minimum retention was observed at low pH near the membrane isoelectric point when charge repulsion is minimal for TFC-S and ESPA4. This was similarly observed by Qin *et al.* [46]. However, retention was mostly pH-independent above pH 5, which suggested that size exclusion was playing a role in addition to charge. The lowest retention was observed with UTC-60, which is the “loosest” membrane. Size exclusion is further supported because NF90 retention for single and mixed feed solutions is similar.

Nitrate retention was generally lower in the presence of the background electrolyte than in purified water (the most notable difference with TFC-S), which has been similarly observed and explained in literature [4, 46]. Because NO_3^- and Cl^- have very similar characteristics (charge, hydrated size and hydration strength, see Table 2), preferential transport of one of the anions with regard to the other with the Na^+ cation would not be expected. However, the increase in Na^+ concentration resulted in enhanced charge shielding and hence reduced retention based on charge repulsion [4, 27, 44, 45]. It is to date unknown if ions such as NO_3^- permeate membranes in hydrated or unhydrated form, which is subject to ongoing investigations.

3.3.3 Fluoride Speciation and Retention

The speciation of fluoride was pH dependent and is shown in Figure 4C. Hydrofluoric acid dissociates at its pK_a of 3.2 to F^- [37]. The chemical equation of the acid dissociation is given in equation (2):



Therefore, above pH 3.2, charged F^- was dominant and above pH 5 all fluoride existed as F^- . Speciation was identical in background solution.

Fluoride retention (shown in Figure 5C and D for single feed solution and Figure 6C and D for mixed feed) was impacted significantly by pH and correlated with speciation. Retention for all membranes, in both purified water and background with single feed, was relatively low at pH 3 (from 5 – 65% depending on membrane and conditions) and increased to 95 – 98% at pH 12.5 with pH. Above pH 7, retention in single feed solutions was > 87% and hence higher than that of either boron or nitrate. In mixed feed solutions, an increase in retention with pH was still observed. High fluoride retention has indeed been observed over a range of conditions in a number of studies [5, 25-28].

This suggested that steric effects contribute to fluoride retention. Although F^- is a very small ion, it is more strongly hydrated because of its high charge density and has a relatively large hydrated radius (0.352 nm, see Table 2) compared to other monovalent anions in solution (0.332 nm for Cl^- and 0.335 for NO_3^-) [5, 28, 47]. Consequently, steric exclusion led to F^- being more strongly retained by tighter membranes. Retention with UTC-60 was very low with a maximum of 53% in MQ at pH 12.5. Because flux decreased with pH, the change in retention could be attributable to either or both changing charge interactions or pore size. Retention with NF90 in single and mixed feed solutions was similar, indicating that size exclusion is important for this membrane.

Near the isoelectric point (pH 3-5), fluoride retention was higher in the presence of background solution (near 70% for BW30 and NF90) than in purified water (< 25%) in the single feed solutions (Figure 5C and D). At acidic pH, fluoride was not retained by UTC-60 and retention by TFC-S was only 5 and 30% for pH 3 and 5, respectively, and approximately 65% for BW30 and NF90. This can be explained with the fact that Cl^- rather than F^- was preferentially transported through the membrane with Na^+ , which is supported both because the hydrated radius of Cl^- is smaller than F^- and because Cl^- is more weakly hydrated (see Gibbs Hydration Energies on Table 2). Interestingly, in the background solution, retention was low at both pH 3 and 5, whereas with purified water, low retention only occurred at pH 3 (this difference is most likely an error). This requires further investigation.

3.4 Conclusions

The objective of this study was to determine the relationship between speciation and retention for boron, fluoride, and nitrate using six different NF/RO membranes. The main conclusions follow:

1. Flux was independent of pH for all membranes except UTC-60, indicating that pH did not alter pore size and hence permeability as well as size exclusion characteristics of those membranes.
2. Boron retention correlated with speciation and was strongly dependent on pH. Below the pK_a of boron ($\text{pK}_a = 9.27$), only $\text{B}(\text{OH})_3$ was present in solution, and retention was generally low and due to the small size of the species. At $\text{pH} \geq 11$, retention for all membranes increased sharply (up to 95%) due to charge repulsion of $\text{B}(\text{OH})_4^-$ from the negative membrane surfaces. The presence of background solution decreased $\text{B}(\text{OH})_4^-$ retention due to charge shielding. The highest boron retention at neutral pH (approximately 50%) was achieved using UTC-80A.
3. The speciation of nitrate was pH independent. Retention varied widely depending on membrane type, and was mostly pH independent above the isoelectric point of the membranes. Data supported that both charge and size mechanisms were occurring. Decreased NO_3^- retention was observed in the presence of background solution due to the screening effects of Na^+ .
4. Fluoride speciation and retention were pH dependent, with minimum retention occurring at low pH when HF dominates (this is similar to what happened with boric acid which is quite interesting!). F^- (ion) was better retained than uncharged HF, due to both charge and size mechanisms. Speciation effects were clearer in single feed solution than mixed feed solution. In single feed solutions, at low pH, fluoride was better retained with the background solution than in purified water, which can be explained by charge and possibly preferential transport of Cl^- rather than F^- to balance the charge of Na^+ .
5. More extensive hydration data is needed for species relevant to this study, and this data is not currently available in the literature. In particular, hydrated radius and Gibbs hydration energies for $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, and HF would be valuable to further elucidate mechanisms. Additionally, pH dependent hydration data is needed for all species.

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Table Captions

Table 1. Membrane properties [48-51].

Table 2. Characteristics of boron, nitrate, and fluoride and other relevant solutes as reported in the literature [35, 47, 52].

Table 1

Membrane (Classification, Manufacturer)	MWCO (Da)	Pore Size (nm)	Material	Functional Groups	Flux*, Pure Water (L.m ⁻² .h ⁻¹)	Flux*, 20 mM NaCl and 1 mM NaHCO ₃ (L.m ⁻² .h ⁻¹)	Isoelectric Point
TFC-S (NF, Koch)	200 [48]	na	polyamide thin film composite	CONH [49]	29.0	25.4	3.1
UTC-60 (NF, Toray)	150 [50]	na	na	na	164	154	3.2
UTC-80A (RO, Toray)	na	na	na	na	10.9	6.9	4.1
BW30 (RO, Filmtec)	98 [51]	0.32	polyamide thin film composite	COOH; amine [51]	17.2	12.1	4.2
NF90 (NF, Filmtec)	100 [51]	0.34	polyamide thin film composite	COOH; amine [51]	54.9	36.6	4.3
ESPA4 (NF, Hydranautics)	na	na	polyamide	na	32.4	18.0	--
na: not available; *Flux, measured at 5 bar							

Table 2

Ion	Molecular Weight (g·mol ⁻¹)	Crystal Radius (nm)	Hydrated Radius (nm)	Gibbs Hydration Energies in Water (kJ·mol ⁻¹)
B(OH) ₄ ⁻	78.84	0.244 [52]	na	na
B(OH) ₃	61.83	na	na	na
Cl ⁻	35.45	0.181 [47]	0.332 [47]	-270 [35]
F ⁻	19.00	0.136 [47]	0.352 [47]	-345 [35]
H ⁺	1.01	--	0.282 [47]	-1015 [35]
HF	20.01	na	na	na
Na ⁺	22.99	0.095 [47]	0.358 [47]	-385 [35]
NO ₃ ⁻	62.00	0.264 [47]	0.335 [47]	-275 [35]
OH ⁻	17.01	0.176 [47]	0.300 [47]	-345 [35]
na: not available				

Figure Captions

Figure 1. Stirred cell system schematic.

Figure 2. Membrane zeta potentials of NF90, UTC-60, TFC-S, BW30, UTC-80A and ESPA4 (in background solution 20 mM NaCl and 1 mM NaHCO₃).

Figure 3. pH dependence of flux for BW30, TFC-S, NF90, ESPA4, UTC60, and UTC-80A in (A) purified water and (B) background solution (20 mM NaCl and 1 mM NaHCO₃).

Figure 4. Speciation for (A) boron; (B) nitrate; and (C) fluoride. Speciation conditions assumed a fixed atmospheric carbonate concentration (partial pressure 3.8·10⁻⁴ atm) and temperature of 25°C.

Figure 5. Single contaminant solutions (5 bar, feed concentrations: 1 mg/L B(OH)₃ as B; 3 mg/L NaF as F; and 100 mg/L NaNO₃ as NO₃⁻): Retention of (A) boron (C) nitrate and (E) fluoride in purified water, (B) boron, (D) nitrate and (F) fluoride in background solution for BW30, TFC-S, and NF90.

Figure 6. Mixed contaminant solutions (5 bar, feed concentrations: 1 mg/L B(OH)₃ as B; 3 mg/L NaF as F; and 100 mg/L NaNO₃ as NO₃⁻): Retention of (A) boron (C) nitrate and (E) fluoride in purified water, (B) boron, (D) nitrate and (F) fluoride in background solution for UTC-80A, ESPA4, UTC-60, and NF90 (background only).

Figure 1

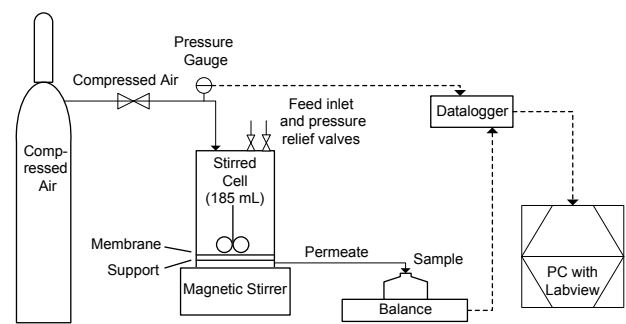


Figure 2

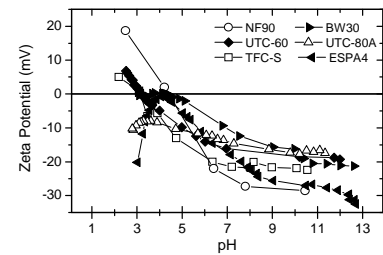


Figure 3

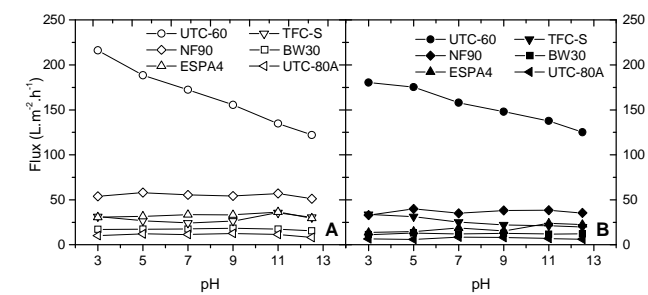


Figure 4

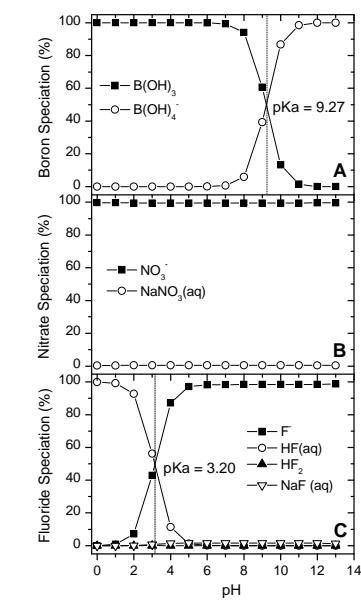


Figure 5

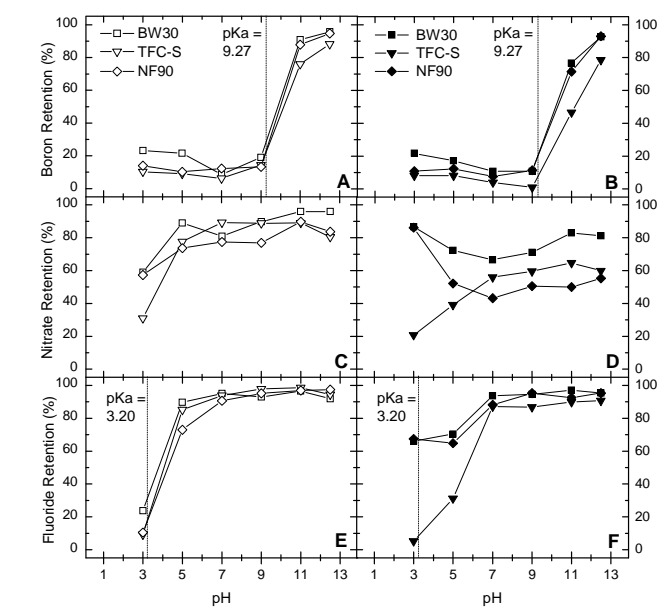


Figure 6

